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ABRASION-RESISTANT SINTERED IRON ALLOYS
[Taimamousei tetsuki shoketsu gokin]

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1. Name of this Invention

Abrasion-resistant Sintered Iron Alloys

2. Claims

[1] Abrasion-resistant sintered iron alloy comprising:

Mo and/or W: 5 - 25%, Cr: 2 - 12%, Si: 0.1 - 0.9%, Mn: 0.7% or less, P: 0.05% or less, C: 0.1 - 1.2%, B: 0.5 - 2.5%, N: 0.002 - 2.0%, and remaining portion: Fe and impure substance.

[2] Abrasion-resistant sintered iron alloy comprising:

Mo and/or W: 5 - 25%, Cr: 2 - 12%, Si: 0.1 - 0.9%, Mn: 0.7% or less, P: 0.05% or less, C: 0.1 - 1.2%, B: 0.5 - 2.5%, N: 0.002 - 2.0%, at least one material selected from V, Nb, Ta, Ti, Zr, Hf, CO, and Ni: 20% or less, and remaining portion: Fe and impure substance.

3. Detailed Explanation of this Invention

[Industrial Field]

This invention pertains to an abrasion-resistant sintered iron alloy used to produce an abrasion-resistant product. For example, the alloy based on this invention can provide excellent abrasion resistance and running-in characteristic when used as a slidable part receiving high surface pressure (e.g., rocker-arm and tappet of

* Numbers in the margin indicate pagination in the foreign text.

internal combustion engine) positioned against a high alloy type camshaft designed to cause abrasions with the counterpart.

[Conventional Technology]

With recent increasing speed and output of internal combustion engine, motion valve parts capable of accommodating such high capacity must be available. Particularly, the area between a camshaft and a rocker-arm or tappet must provide extremely high durability against sliding motions.

Generally speaking, since the section of rocker arm or tappet receiving sliding motions of a camshaft receives a high surface pressure, such area must have strong abrasion resistance, scuffing resistance, and pitting resistance, with sufficient running-in characteristic. /226

Therefore, developers of this invention investigated a method to provide an improved sintered iron alloy with sufficient abrasion resistance and reported the following alloy (refer to Patent No. 61-54150).

Mo and/or W: 5 - 20%, Cr: 2 - 10%, Si: 0.1 - 0.9%, Mn: 0.7% or less, P: 0.05% or less, C: 0.1 - 0.8%, B: 0.5 - 2%, and at least one material selected from V, Nb, Ta, Ti, Zr, Hf, CO, and Ni: 20% or less, and remaining portion: Fe and impure substance.

[Problems to Be Solved by this Invention]

The abrasion-resistant sintered iron alloy described above provides excellent abrasion resistance, scuffing resistance, and

pitting resistance with a running-in characteristic against the counterpart. Therefore, when used with a rocker-arm or tappet in the standard setting, the alloy is highly effective.

However, in order to carry out high capacity and high-speed operation of rotation engine, valve must be designed as multi-valve part containing an increased number of camshafts with reduced diameters and increased cam lift capacities. To satisfy this conditions, high alloy cam (camshaft) becomes necessary. When the sintered iron alloy reported in Patent No. 61-54150 is used for a long period in such setting, the abrasion-resistance may become inadequate.

[Purpose of this Invention]

To provide an alloy durable enough as a counterpart of a high alloy type cam (camshaft), that can maintain excellent abrasion resistance after a long period of use, the developers of this invention investigated a technique to reinforce and harden carbide, borate, and carbon borate by conducting various experiments. As a result, they discovered that the following steps could drastically improve the abrasion resistance of the alloy without negatively affecting the benefits of the alloy: (1) By increasing the amounts of Mo, W, Cr, etc., and adding nitrogen to the mixture, a nitride having excellent affinity to carbide and borate can be deposited; then, (2) a portion of carbide, borate, or nitride is substituted and/or made into a solid solution, and/or arranged to coexist.

Particularly, since fine carbide and borate coexist in the system during sintering process, by adding nitrogen to the system, a nitride can easily form a solid solution or substitution with carbide and borate.

[Constitution of this Invention]

[Method to Solve the Problems]

The first claim of this invention provides an abrasion-resistant sintered iron alloy comprising:

Mo and/or W: 5 - 25%, Cr: 2 - 12%, Si: 0.1 - 0.9%, Mn: 0.7% or less, P: 0.05% or less, C: 0.1 - 1.2%, B: 0.5 - 2.5%, N: 0.002 - 2.0%, and remaining portion: Fe and impure substance.

With the second claim of this invention, in addition to the configuration described in the first claim, at least one material selected from V, Nb, Ta, Ti, Zr, Hf, CO, and Ni is included for an amount of 20% or less.

[Operation]

With the abrasion-resistant sintered iron alloy consisting of the composition described above, fine carbide, borate and/or carbon borate are uniformly dispersed during the sintering process, being able to function as nuclei or intermediate media. Therefore, since the composition also contains nitride, fine carbon nitride, boric nitride and/or solid solution/partly substituted material can be created as uniformly deposited stable and fine substances, without forming bulky compositions.

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Among the alloys that can be created by this method, an alloy containing a sufficient amount of fine double carbide, double borate, double nitride and/or carbon borate, carbon nitride, boric nitride and/or solid solution of those material in its matrix was found to provide excellent sliding-resistance and abrasion-resistance. Such alloy was found to produce exceptionally effective abrasion resistance and running-in characteristic when applied to the sliding area of rocker-arm or tappet having a counterpart that is a high alloy camshaft having a severe cam profile.

[Basis on the Specified Amount Range of Each Substance]

The following explains the reason for setting the range of each composition material (wt%).

Mo and W:

Mo and W bond to C, B, and N in the composition with Fe and Cr to form double carbide, double borate, double nitride, or a part substitution or solid solution of those double materials, providing excellent abrasion-resistance, where some portion becomes a solid solution in a matrix to reinforce the matrix while increasing the annealing hardness. However, if the amount is less than 5%, said effectiveness cannot be sufficiently manifested to cause insufficient abrasion-resistance. On the other hand, amount exceeding 25% results in saturated effectiveness and is uneconomical. Therefore, the content ratio should be 5 - 25%.

Cr :

Cr forms double carbide, double borate, and double nitride with Fe, Mo and W to increase the abrasion-resistance, and at the same time, becomes a solid solution in the matrix to increase the sintering characteristic, durability against annealing, and corrosion-resistance of the matrix. However, if the amount is less than 2%, said effectiveness cannot be sufficiently manifested. On the other hand, amount exceeding 12% results in saturated effectiveness, and rather worsens the mechanical strength and increases its resistance against the counterpart. Therefore, the content ratio should be 2 - 12%.

Si:

If the amount of Si is less than 0.1 %, deoxidation effect becomes minimal, subsequently leaving a large amount of oxygen in the powder, worsening the sintering characteristic. Also, a bulky plate-like M_2C type carbide tends to be deposited to lower the running-in characteristic with the counterpart. On the other hand, amount exceeding 0.9% results in saturation of effectiveness, and rather causes increased particle roundness to lower the molding characteristic. Therefore, the content ratio should be 0.1 - 0.9%.

Mn:

Mn, which has a deoxidation effect like Si, can reduce the oxygen content in the powder to increase the sintering characteristic. However, an amount exceeding 0.7% rather increases particle roundness to lower the molding characteristic, leading to

chipping of mold product. Therefore, the content ratio should be 0.7% or less.

P:

0.2 - 0.8% of P is commonly used as a sintering acceleration element for sintering an abrasion-resistant alloy. However, an amount exceeding 0.05% in the sintered alloy based on this invention results in bulky double borate, double carbide, and carbon nitride, which reduces the running-in characteristic for the counterpart. In addition, double borate and double carbon borate precipitate and form a network-like structure around the particle boundary to reduce the strength. Therefore, the content ratio should be 0.05% or less.

C:

C partially bonds to carbide-forming elements (e.g., (Mo, W, Cr, V, etc.) to create a double carbide. Also, it is partially substituted with N in nitride to form carbon nitride. Furthermore, it creates carbon borate with boron. By forming those compositions, C can improve the abrasion resistance, while remaining C can form a solid solution in the matrix to increase the hardness and strength at room temperature. However, an amount less than 0.1% results in insufficient quantities of double carbide, carbon nitride, carbon borate, which leads to inadequate hardness of matrix at room temperature, thereby resulting in insufficient abrasion-resistance. On the other hand, an amount exceeding 1.2% results in coagulated double carbide and carbon nitride to form bulky carbon borate,

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subsequently increasing fragility of the material. Also, running-in characteristic decreases. Therefore, the content ratio should be 0.1 - 1.2%.

This C element is preferably added in a form of vacuum-sintered Fe-Mo-W-Cr-V-Si-(Mn)-(Co)-(N)-C type atomized alloy powder. This is because, if C alone is added as graphite power, it tends to bond to Fe-B or Fe-Cr-B added as the source of B (described later) and makes bulky carbon borate deposited along the particle boundary in a form of network during sintering process to increase the offensive nature against counterpart.

B forms double borate with Mo, W, V, Cr, and Fe in the composition to increase the abrasion-resistance and running-in characteristic. Also, a portion of B forms a solid solution in the matrix to improve the sintering characteristic. In addition, a part of double borate bonds or substitutes C and N to form a double carbon borate and double boron nitride, which then increase the abrasion-resistance.

Thus, B, which forms fine double borate, double carbon borate, and double boron nitride, is an essential main substance for improving the abrasion-resistance and running-in characteristic of the sintered alloy based on this invention. However, an amount less than 0.05% cannot provide sufficient effectiveness, whereas an amount exceeding 2.8% results in saturated effectiveness, and rather forms

bulky double borate to lower the running-in characteristic for the counterpart. Therefore, the content ratio should be 0.5 - 2.5%.

Amount of B additive in the sintered alloy based on this invention should be within a range of 0.5 - 2.5% as described above, where the best effect can be obtained when the amount satisfies:
$$[\text{Mo} + \text{W content (atomic quantity)}] / [\text{B content (atomic quantity)}] = 0.8 - 1.5.$$
 This is because, when the atomic ratio exceeds 1.5, an amount of double borate product becomes too small to maintain the running-in characteristic of the alloy. Also, an amount less than 0.8 results in bulky borate double which tends to be deposited in the particle boundary, forming a network, subsequently reducing the running-in characteristic and own pitting characteristic. To add 'B' element, Fe-B or Fe-Cr-B type alloy powder is preferably used.

N:

N bonds to the metallic elements in the composition to form a double nitride. Then, N, B and C in the double nitride are substituted and bonded to form a double carbon nitride and boric nitride double to provide an abrasion-resistance and running-in characteristic. Also, a part of such compound forms a solid solution in the matrix to improve the corrosion-resistance. However, if the content is less than 0.02%, the amount of double nitride is too small to provide sufficient abrasion-resistance; whereas an amount exceeding 2.0% results in creating bulky double nitride to increase the fragility of the alloy while lowering the running-in

characteristic against the counterpart. Therefore, the amount should be 0.002 - 2.0%. In this case, nitrogen may be included in the matrix powder. Also, it may be added in a form of VN, BN, or NbN powder.

Al:

Al is an element heightening the nitride hardness. Although an amount exceeding 0.05% can provide notable effectiveness, an amount exceeding 1.0% prevents smooth sintering by lowering the density of the nitride. Therefore, when added to increase the nitride hardness, the amount should be within a range of 0.2 - 1.0%.

V, Nb, Ta, Ti, Zr, Hf, Co, Ni:

V, Nb, and Ta forms extremely hard double carbide, double nitride, and double carbon nitride by bonding to C and N. Also, it forms a double carbide, double borate and double nitride by substituting a part of Mo and W to provide abrasion-resistance. In this case, a portion of such substances forms a solid solution in the matrix to strengthen the matrix while increasing the annealing hardening. Also, V, Nb, and Ta prevent the formation of bulky crystal grains and bulky carbide during sintering. Those benefits are not noticeable when the total amount of V, Nb, and Ta is less than 0.5%, and rather they lower the abrasion-resistance and strength. On the other hand, an amount exceeding 8% results in saturated effectiveness and is uneconomical. Therefore, the content should be 0.5 - 8%.

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Ti, Zr, Hf, and Co are borate-formation elements and can effectively improve the abrasion-resistance. Therefore, 12% or less quantity is allowable. Particularly, Co substitutes a portion of Mo and W to form a double, and also, forms a solid solution in the matrix to improve the hardness in the red heat. Therefore, adding this element is particularly effective when the abrasion-resistance is needed in the heat.

Furthermore, N may be added within a range not causing austenite matrix. This is because Ni, being able to improve the corrosion-resistance of matrix can be effectively added to produce a part, receiving strong corrosive abrasion (e.g., rocker-arm for EGR-diesel engine and oil pressure lifter).

The hardness of sintered alloy consisting of the composition described above is preferably within a range of 50 - 70 H_RC. If it is less than 50 H_RC, abrasion resistance becomes insufficient, whereas hardness exceeding 70 H_RC results in weak running-in characteristic.

Also, the theoretical density ratio of sintering alloy should be 90% or higher. This is because, the theoretical density ratio below 90% results in weak matrix with large air holes. The cutting-off function of air holes tends to destroy the matrix to easily cause pitting abrasion.

Operational example:

The following explains the operational example of this invention of abrasion-resistant sintered iron alloy and a comparison example.

As raw powders, vacuum-annealed 100 mesh Fe-Cr-Mo-W-Si-C type atomized alloy powder (may contain V, Nb, Ta, Co, and N if necessary), -325 mesh Fe-Mo powder or pure W powder, -250 mesh Fe-B alloy powder (B: 20%), -250 mesh Fe-P alloy powder (P: 26%), -250 mesh ferro-titanium, ferro-zirconium, and ferro-hafnium alloy powders, -325 mesh carbonyl Ni powder, and -500 mesh TiN, NbN, VN, BN, and AlN were made into various compositions shown in Table 1. Also, as a lubricant, high class fatty acid was added and mixed. Each prepared powder was molded to form a pressed powder using a pressure of 7 ton/cm². Next, after this pressed powder was annealed at 1150°C - 1250°C for 60 minutes in a non-oxidation atmosphere, a heat process was performed to prepare Operational example alloys No. 1 - No. 18 and Comparison example alloys NO. 1 - No. 10.

Next, each of prepared alloys was applied to the area sliding against a camshaft of internal rush adjuster type rocker-arm, and built into a V-type 6-cylinder gasoline engine to perform capacity evaluation tests. The camshaft was made of high alloy chilled molded material which was composed of (wt%):

C: approx. 3.7%, Si: 2.0%, Mn: 0.7%, Mo: 1.0%, Cr: 1.2%, V: 0.2%, Ti: 0.1%, P: 0.2%, Cu: 0.5%, and Fe: remaining amount.

The hardness was 58 H_RC or higher. In this case, the camshaft is high output/lift type, containing high speed opening/closing valves, designed to prevent oil film formation.

The capacity evaluation tests were conducted under the following conditions:

Engine rotation count: 600 rpm, oil: approx. 25,000 Km run recycled oil for gasoline engine, oil temperature: 60°C, operational time: 800 hours; other operational conditions were same as the actual operation conditions.

An abrasion test was conducted under the conditions described above to measure the abrasion at the sliding area of rocker-arm and abrasion of cam area of the camshaft, which was the counterpart. Also, scuffing and pitting occurrence during sliding were observed. The results are shown in Table 1.

With the results of Comparison alloy No. 1 - No. 10 in Table 1, /230 as amounts of composition elements do not satisfy the ranges specified by this invention, excessive abrasion as well as scuffing and pitting occur at the rocker-arm and camshaft, thereby not being able to provide satisfactory outcomes.

On the other hand, with the results of Operational alloy No. 1 - No. 18, every alloy showed excellent abrasion resistance, not causing any significant damage to the cam area, thus providing excellent scuffing/pitting resistance.

Note that each operational alloy described above was heat-treated to provide a matrix system mainly consisting of annealed marten sites. However, by appropriately selecting this heat-

processing conditions, the matrix system can be made into bentonite, pearlite, or bentonite + pearlite system.

Table 1

Table 1

(a)	(d)	(f)	(g)	(e)	(h)	(j)	(k)	(l)	(m)	(n)	(o)	(p)	(q)	(r)																									
区分		成分組成 (重量%)		性能評価結果		(i)		(j)		(k)		(l)		(m)		(n)		(o)		(p)		(q)		(r)															
		No.	Fe	Si	Mn	Cr	Ni	P	C	S	Al	V	Nb	Ti	Zr	Hf	Co	W	Mo	Cu	Zn	Pb	Sn	Ag	Au														
本機 明 実 施 例 合 計	No.	1	9.5	4.2	4.8	0.7	0.5	0.02	1.1	0.9	0.05	-	-	-	-	-	-	-	-	0.062	0.046	(i)	正常 スカフティングおよび ビッチングともなし	(j)	(k)	(l)	(m)	(n)	(o)	(p)	(q)	(r)							
		2	4.9	10.0	5.0	0.5	0.4	0.02	0.0	0.0	0.7	-	-	-	-	-	-	-	-	0.048	0.052																		
		3	10.0	5.0	7.9	0.0	0.0	0.04	0.4	1.0	1.0	-	-	-	-	-	-	-	-	0.045	0.053																		
		4	9.0	3.0	10.0	0.0	0.0	0.04	0.5	1.0	0.5	-	-	-	-	-	-	-	-	0.043	0.051																		
		5	10.0	5.0	8.0	0.6	0.4	0.04	0.0	0.0	1.5	-	-	-	-	-	-	-	-	0.037	0.042																		
		6	7.0	4.0	3.0	0.5	0.0	0.02	0.7	0.7	0.03	-	-	-	-	-	-	-	-	0.040	0.022																		
		7	0.1	5.0	7.5	0.5	0.4	0.02	0.7	0.0	0.1	0.10	1.0	-	-	-	-	-	-	0.015	0.017																		
		8	12.0	5.0	5.0	0.4	0.4	0.02	0.0	1.2	1.5	0.06	-	-	-	-	-	-	-	0.020	0.040																		
		9	10.0	5.0	8.0	0.6	0.4	0.02	0.0	1.0	0.05	0.07	-	-	-	-	-	-	-	0.040	0.020																		
		10	10.0	7.0	10.0	0.7	0.0	0.02	0.7	1.0	0.2	0.15	-	-	-	-	-	-	-	0.025	0.045																		
		11	4.0	3.0	3.0	0.5	0.4	0.02	0.0	0.0	0.1	0.20	1.5	-	-	-	-	-	-	0.030	0.020																		
		12	5.0	4.0	8.0	0.5	0.5	0.02	0.1	1.0	0.1	0.10	-	-	-	-	-	-	-	0.040	0.040																		
		13	5.0	4.0	7.0	0.5	0.4	0.02	1.0	1.0	0.1	0.07	-	-	-	-	-	-	-	0.037	0.042																		
		14	5.0	4.0	7.0	0.4	0.4	0.03	0.3	1.0	0.15	0.12	-	-	-	-	-	-	-	0.056	0.020																		
		15	5.0	4.0	7.0	0.0	0.5	0.02	0.5	1.2	0.15	0.10	-	-	-	-	-	-	-	0.035	0.010																		
		16	5.0	4.0	7.0	0.5	0.5	0.03	0.7	0.0	0.1	0.08	0.5	1.0	-	-	-	-	-	0.020	0.042																		
		17	12.0	0.0	10.0	0.7	0.0	0.02	0.0	1.2	0.1	0.06	0.2	0.2	0.1	-	-	-	-	0.010	0.037																		
		18	5.0	1.0	3.0	0.2	0.2	0.01	0.2	0.0	0.02	0.07	2.0	2.0	0.0	0.05	0.3	0.5	0.1	0.05	0.052																		
比 較 例 合 計	No.	1	10.0	1.0	7.0	0.4	0.4	0.02	0.5	0.0	-	-	0.5	-	-	-	-	-	0.030	0.052	(j)		(k)		(l)		(m)		(n)		(o)		(p)		(q)		(r)		
		2	12.0	0.0	5.0	0.4	0.4	0.02	0.0	1.0	-	-	0.5	0.5	-	-	-	-	0.070	0.005	ロッカーアームチップスカフティングあり カム厚は最大 ロッカーアームチップスキュークエックあり ロッカーアームチップスキュークエックあり ロッカーアームチップスキュークエックあり ロッカーアームチップスキュークエックあり ロッカーアームチップスキュークエックあり ロッカーアームチップスキュークエックあり ロッカーアームチップスキュークエックあり ロッカーアームチップスキュークエックあり ロッカーアームチップスキュークエックあり		(k)		(l)		(m)		(n)		(o)		(p)		(q)		(r)		
		3	11.0	0.0	6.0	0.0	0.4	0.02	0.0	1.0	1.0	2.0	2.5	-	-	-	-	-	0.050	0.107																			
		4	10.0	7.5	6.0	0.4	0.3	0.02	0.7	1.0	0.01	0.20	-	-	-	-	-	-	0.075	0.050																			
		5	4.0	4.0	2.0	0.0	0.0	0.02	0.7	1.0	0.5	1.00	-	-	-	-	-	-	0.050	0.080																			
		6	5.0	4.0	8.0	0.5	0.4	0.02	0.7	1.0	4.0	1.00	-	0.5	-	-	-	-	-	0.060	0.120																		
		7	20.0	10.0	7.0	0.4	0.4	0.02	0.5	1.2	0.2	0.07	-	-	-	-	-	-	-	0.072	0.100																		
		8	10.0	0.0	20.0	0.0	0.2	0.02	0.7	0.0	0.2	-	-	-	-	-	-	-	-	0.065	0.120																		
		9	11.0	4.0	0.0	0.3	0.4	0.02	0.0	0.0	0.1	0.10	-	-	-	-	-	-	-	0.125	0.030																		
		10	10.0	0.0	7.0	0.2	0.5	0.04	0.7	0.0	0.1	0.10	-	-	-	-	-	-	-	0.120	0.070																		

Key: (a) Section; (b) Operational example alloy; (c) Comparison example alloy; (d) Element composition (wt%); (e) Capacity evaluation result; (f) Rocker arm abrasion depth; (g) Camshaft abrasion depth; (h) Rocker arm camshaft appearance; (i) Residue Normal (No scuffing or pitting); (j) Rocker arm chips/cuffing; (k) Maximum rocker arm chip abrasion; (l) Rocker arm chips edge-cracks; (m) Rocker arm chips/cuffing; (n) Rocker arm chip/edge cracks; (o) Rocker arm chip/pitting exist/cam-scuffing exists; (p) Maximum cam abrasion; (q) Rocker arm chip/pitting exist with maximum cam abrasion; (r) Large rocker arm chips/cuffing; (s) Large rocker arm chips/pitting

Also, although operational alloys were applied to sliding parts of the rocker-arms in the example, they may be used in the area of receiving high surface pressure, requiring boundary surface lubrication or dry abrasion (e.g., tappet, cam, sleeve, and valve sheet).

[Effectiveness of the invention]

As explained above, the first claim of this invention provides an abrasion-resistant sintered iron alloy comprising: Mo and/or W: 5 - 25%, Cr: 2 - 12%, Si: 0.1 - 0.9%, Mn: 0.7% or less, P: 0.05% or less, C: 0.1 - 1.2%, B: 0.5 - 2.5%, N: 0.002 - 2.0%, Al (added to increase the nitride hardness if necessary), and remaining portion: Fe and impure substance. Also, with the alloy based on the second claim of this invention, in addition to the configuration described in the first claim, at least one material selected from V, Nb, Ta, Ti, Zr, Hf, CO, and Ni is included for an amount of 20% or less. /231

Therefore, any alloy consisting of the compositions described above contains a sufficient amount of fine carbide, borate, nitride and/or carbon borate, carbon nitride, and/or solid solution of those material in its matrix system as a uniformly dispersed system. Therefore, they can provide excellent sliding-resistance and abrasion-resistance. Such material was found to produce exceptionally effective abrasion resistance and running-in characteristic even after used for a long period as sliding area of rocker-arm or tappet friction against a high alloy type camshaft having a severe friction profile. Therefore, this invention can provide significant benefits to the related industry.